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Presented at
EPA/EPRI
NINTH SYMPOSIUM ON
FLUE GAS DESULFURIZATION
Cincinnati, Ohio
June 4-7, 1985

TP 85-48
FX/CSG

STONE & WEBSTER ENGINEERING CORPORATION
BOSTON, MASSACHUSETTS

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ABSTRACT

The use of dibasic acid (DBA) in a flue gas desulfurization (FGD) system buffers the scrubber chemistry, resulting in increased scrubber SO_2 removal efficiency. The use of DBA may also result in reduced scrubber electricity consumption. It is expected that Indianapolis Power & Light Company's (IPL) Petersburg Unit 3 can burn higher sulfur coal when using DBA in the scrubber, while maintaining its current 30-day average SO_2 control. However, long-term effects of factors that may limit scrubber performance (e.g., demister pluggage or dewatering equipment performance) have yet to be determined. Other effects of DBA addition, such as increased corrosion rates, also must be considered in long-term use of DBA.

The use of DBA at Petersburg Unit 3 did not reduce limestone consumption. The use of DBA on an annual basis or on an "as-needed basis" may result in increased scrubber reliability in that scrubber SO_2 emission excursions may be minimized. In addition, operation of the scrubber with DBA, lower booster fan inlet vane settings, and continued use of presently available coal should result in increased scrubber reliability because wet gas recirculation to the booster fans will be minimized.

PURPOSE AND SCOPE

The purpose of the process evaluation and the additive test program initially was to establish the FGD system baseline conditions and then determine the effect of a buffer additive on improving SO_2 removal and system reliability, and reducing demister scale formation. A major goal of the process evaluation also was to determine the limestone quality, grind, and slurry concentration.

Specific reasons for the additive tests are as follows:

- Determine percent sulfur coal that can be burned without exceeding allowable emissions
- Document FGD system process data
- Optimize limestone grinding circuit
- Evaluate use of buffer additive agent

The quantitative results were measured by changes in SO_2 removal, limestone consumption, waste characteristics, operating costs, demister section solids accumulation, and other parameters.

The Stone & Webster Engineering Corporation (SWEC) project included engineering, design, procedures, scheduling, purchasing, delivery, inspection, observation, checkout, training, sampling, testing, monitoring, analytical activities, evaluation, data reduction, and report preparation.

DESCRIPTION OF SWEC/IPL LABORATORY

The chemical analyses of samples collected during the entire test period (June 11 to August 24, 1984) were performed by various companies under the direction of SWEC. A description of these various laboratory facilities is as follows:

DBA TEST AND PROCESS EVALUATION EQUIPMENT

SWEC arrived onsite at Petersburg Unit 3 for an internal inspection on May 5, 1984, and set up a scrubber laboratory trailer.

This laboratory equipment, used during the entire test program, became the property of IPL when SWEC left the site on August 25, 1984.

COMMERCIAL TESTING COMPANY LABORATORY

SWEC employed Commercial Testing & Engineering Company (CTE) of Henderson, Kentucky, to perform some chemical analyses. The FGD samples were sealed in plastic bottles or bags and picked up by CTE.

IPL COAL LABORATORY

IPL operated a coal laboratory at the Petersburg Generating Station. IPL collected coal samples at each of the operating pulverizer outlets of Unit 3 and analyzed for sulfur using a LECO sulfur determinator. This sulfur information was given to SWEC for use during the test program. In addition, IPL prepared a composite coal sample (from all operating pulverizer outlets) which was given to SWEC for moisture, sulfur, and/or ultimate analyses.

MONSANTO CHEMICAL COMPANY

IPL employed Monsanto Chemical Company to perform DBA test on analysis work at their analytical laboratory, located in Gonzales, Florida.

ACUREX CORPORATION

SWEC employed Acurex Corporation to provide DBA chemistry consultation (Dr. J. Chang) and scrubber inlet flue gas testing. Acurex provided input into the chemistry of DBA and provided flue gas sampling and reports.

INDUSTRIAL CONTRACTORS

IPL employed Industrial Contractors to field assemble the DBA test equipment. SWEC provided equipment field checkout, startup, and personnel training.

LOG OF SAMPLES TAKEN DURING ENTIRE TEST PERIOD

SWEC took over 1000 samples while onsite during May 5 to August 24, 1984. Each sample was entered into a log of samples.

BUFFER ADDITIVE STORAGE AND INJECTION SYSTEM

SWEC and IPL designed and operated the temporary buffer agent additive delivery, storage, and injection system. The buffer agent additive tests were performed July 23 to August 24, 1984, using a Monsanto DBA mixture as the buffer agent additive. The DBA mixture is a water solution of adipic, glutaric, and succinic acids, which also contains a small amount of nitric acid. This mixture was delivered, stored, and added to the Petersburg Unit 3 FGD system as a 25 percent DBA by weight solution.

DBA DELIVERY

Twenty-five percent DBA solution at approximately 110°F was delivered to the Petersburg site from the Monsanto adipic acid manufacturing facility in Pensacola, Florida. Deliveries were made by McKenzie Trucklines in 40 ft x 8 ft x 12 ft, 5,000 gal, insulated stainless steel trailers which were backed into the unloading area in the vicinity of the electrical building opposite Module B. The McKenzie trailers used for transporting DBA had bottom unloading ports equipped with double shutoff valves and 3-inch quick-connect fittings. Each trailer arrived onsite with sufficient hose, fitted with 3-inch quick-connect fittings, so that the DBA could be unloaded into the storage trailer through the hatch located midpoint in the storage trailer top. Each delivery trailer tractor was equipped with its own self-contained transfer system, with an unloading capability of approximately 100 gpm.

DBA STORAGE

The trailer contents were transferred by self-contained equipment into the 6,700 gal insulated stainless steel. Storage trailer located in the vicinity of Module A, which was in close proximity to the IPL laboratory trailer and the buffer agent additive injection pump. The trailer was equipped with a standard manway, which facilitated access to the top of the trailer. In order to ensure that an adequate inventory of DBA was maintained throughout the test, the deliveries were closely coordinated with the test operation. The trailer discharge port (equipped with emergency hydraulic shutoff valve, a manual shutoff valve, and a 3-inch quick-connect male connection) was connected to the start of the hard-piped injection pump suction system (equipped with female connection) by a hose with 3-inch quick-connect fittings. Recirculated solution from the DBA injection system was returned to the storage trailer through the hatch located on top of the trailer.

TEMPORARY DBA INJECTION SYSTEM

The temporary DBA injection system consisted of a Gould injection pump, a pump suction piping system, a pump discharge and distribution piping system and a recirculation system, which returned the major portion of the pump discharge liquor to the storage trailer. All wetted surfaces in this system were either 316 or 316L stainless steel or materials having comparable corrosion resistance. The pump suction system consisted of:

- A 3-inch quick-connect female fitting to accept the 3-inch quick-connect male fitting attached to the storage trailer discharge hose
- A 3-inch to 1 1/2-inch reducer
- The following 1 1/2-inch size items: in-line strainer, shutoff gate valve, bimetallic thermometer with fitting, water flush system, and necessary pipe and fittings

Discharge from the Gould centrifugal injection pump was either pumped to the FGD system or recirculated to the storage trailer through 1-inch pipe. Under test design conditions, 25 percent (by weight) concentration DBA solution was added to the FGD system to maintain the DBA concentration. The remaining 85 to 90 gpm of liquor was returned to the storage tank. Control of the two streams was maintained by globe valves located in the recirculation line and in the FGD system feedline. The two valves were located in close proximity to the pump, to each other, and to the Badger oscillating piston totalizer meter located in the FGD system feedline.

The DBA solution was distributed to the four modules through individual rotameters and module downcomer injection ports. Bypass capability with the necessary valves was provided around each rotameter to permit servicing of the rotameters and addition of DBA, on a slugging basis, to each module. Slugging was necessary when large increases in FGD system DBA concentration were required, e.g., increasing the DBA concentration from 500 ppm to 1,000 ppm prior to the 1,000 ppm test period. Water flush capability for the recirculation, FGD system feed, and distribution systems was provided.

OPERATING AND MAINTENANCE PROCEDURE WITH DBA

There were two modes of test operations, 1) the constant addition of a relatively small amount of DBA to the FGD system using individual module rotameters and 2) the slugging of a larger amount of DBA to individual modules to provide gross increase in FGD system DBA treatment levels. For the addition of larger quantities of DBA, the rotameter(s) were bypassed and the addition amount was measured by the totalizer.

The flow of DBA to the individual modules required adjustments based on actual analyses of FGD system DBA concentration levels.

DBA crystal formation in the 25 percent DBA solution did not occur because the solution temperature did not drop below 70°F. Recirculation of the bulk of the liquor into the storage tank and the relatively quick turnover maintained pump discharge temperatures in excess of 110°F (e.g. 110°F to 140°F). DBA temperature levels in the individual module injection systems were checked at the rotameter calibration lines. The individual injection systems were flushed with water into the FGD system modules.

Maintenance procedures were as prescribed in the Gould, Badger, and Wallace and Tiernan instruction brochure provided with the totalizer, pump, and rotameters, respectively.

SWEC, Monsanto, and IPL trained over 30 IPL personnel in the safe O&M and safety considerations of the DBA system and laboratory procedures.

BUFFERING AGENT ADDITIVE TEST PROGRAM

SWEC performed buffering agent additive tests, along with specific sampling, monitoring, and analytical work, from July 23 to August 24, 1984. During this time period, both normal sulfur and high sulfur coals were burned. The tests were performed as follows:

- During the week of July 23, 1984, SWEC tested approximately 500 ppm buffering agent additive concentration in the absorber recycle tank, at a pH of approximately 5.7 to 5.8, to determine the effect of a moderate concentration of buffer agent at a moderate pH.

- During the week of July 30, 1984, SWEC tested approximately 1000 ppm buffering agent additive concentration in the absorber recycle tank, at a pH of approximately 5.7 to 5.8, to determine the effect of increased buffer agent additive at a constant pH.

- During the week of August 16, 1984, SWEC tested approximately 500 ppm buffering agent additive concentration in the absorber recycle tank, at a pH of approximately 5.2 to 5.3, to determine the effect of a moderate concentration of buffer agent at a low pH.

- During the last weeks of testing, August 13 and August 20, 1984, SWEC maintained approximately 1000 ppm DBA, at a pH of approximately 5.8 (the optimum buffering agent additive concentration and pH as determined by previous testing), to obtain long-term test results.

- During the last two days of testing, SWEC increased the DBA concentration to approximately 2000 ppm, at a pH of approximately 5.8, to document the effects of high DBA concentration on SO_2 removal.

Detailed written test and analytical procedures were adhered to during the test period. Appendix I presents the procedures for DBA concentration by titration. Figure 1 shows typical titration curves for deionized water, and filtered recycle tank slurry with and without DBA.

BUFFERING AGENT ADDITIVE TEST RESULTS

This section presents a summary of scrubber performance data collected during the DBA test period. The following is a description of the parameters:

- Unit 3 Load-MW gross was taken from the computerized Daily Summary for that day.

- Sulfur in coal was presented from composite samples of the mills in service and sent to Commercial Testing & Engineering (CTE). Percent sulfur basis was as sampled from mills.

- Booster fan inlet vane settings were actual board readings taken by SWEC.

- SO_2-stack monitor (ppmv wet) were taken from the stack monitor recorder.

- Adipic acid equivalent concentration was ppm by weight.

- Solids in slurry-recycle tank readings were taken by hydrometer or percent solids analyses.

- Lb $SO_2/10^6$Btu, FGD system in/out: Inlet value was based on fuel sulfur analysis and calculation of HHV by Dulong equation (from coal ultimate analysis). Stack 3-hour averaged values were determined by using IPL equation and the SO_2 and CO_2 3-hour averaged values from the computerized daily emission logs.

- Module SO_2 removal was based on KVB monitor scrubber inlet/outlet readings. Modules A and B efficiencies were based on booster fan BFF-3-1 outlet duct readings, and Modules C and D efficiencies were based on BFF-3-2 outlet duct readings (inlet to scrubber).

- Stoichiometry (defined as Moles $CaCO_3$ added to scrubber per mole of SO_2 removed) was calculated from chemical analysis of Recycle Tank B slurry. Filter cake analyses were also used to estimate stoichiometry, but these were delayed by the residence time in the thickener.

- Sulfite-to-sulfate ratios were calculated from chemical analyses of Recycle Tank B and filter cake samples. Recycle tank slurry was used for this information.

- Limestone purity was obtained by chemical analyses.

CONSUMPTION OF DBA

Table 1 presents a summary of the DBA shipments received July 19 to August 23, 1984, at Petersburg Unit 3. During the SWEC DBA test period, the total amount of DBA used was approximately 75,000 lb (on a dry weight basis). The daily average gross generation during this period was 9,590 MWh, and the daily average SO_2 removed by the entire FGD system was 169 tons. The daily average DBA concentration in the scrubber modules was 730 ppm by weight adipic acid equivalent. Therefore, during the SWEC DBA test period, the consumption of DBA on a dry weight basis was as follows: 2,310 lb DBA/day, 0.24 lb DBA/MWh, and 13.6 lb DBA/ton SO_2 removed by the FGD system.

The usage of DBA at Petersburg, from August 13 to August 16, 1984, was determined. During this four-day period, the total amount of DBA solution used was approximately 5,200 gal, which is equivalent to 11,060 lb of DBA on a dry weight basis. The daily average gross generation was 10,360 MWh and the daily average SO_2 removed by the entire FGD system was 226 tons. As presented in Table 2, the daily average DBA concentration in the scrubber modules was 960 ppm by weight adipic acid equivalent. Therefore, during this high sulfur coal (approximately 3 percent sulfur) and 1,000 ppm DBA test period, the consumption of DBA on a dry weight basis was as follows: 2,760 lb DBA/day, 0.27 lb DBA/MWh, and 12.2 lb DBA/ton SO_2 removed by the FGD system.

UPPER DEMISTER SOLIDS ACCUMULATION

Upper demister solids accumulation and resulting plugging was a continuing problem. If not controlled, the pluggage would result in restricted gas flow through the absorber modules and inability to treat sufficient flue gas as originally designed.

To quantify scale accumulation under different test situations, 20 upper demister sections were numbered with plastic tags and weighed to estimate solids accumulation rates. Each reinforced fiberglass demister section was weighed a minimum of three times and the weights were averaged. The average solids accumulation rate without any treatment was 0.732 lb/day. With DBA in the recycle tanks (and DBA eventually in the demister wash water reclaimed from the thickener), the rate was 1.518 lb/day. These results were inconclusive for the following reasons:

- The location of a demister section in the absorber vessel affects accumulation of solids. Due to nonuniform gas flow, uneven distribution of demister wash water, and uneven pluggage of the lower demisters, some areas of the upper demister were clean and others were entirely plugged across the vanes in a single absorber vessel.

- Accumulation of solids occurred in two distinct mechanisms ways--hard crystalline scale and soft slurry solids--either or both of which may be present in different areas of the same module's upper demister or on the same demister section.

- Burning high sulfur fuel (resulting in higher velocities of gas in the modules) for various lengths of time for the three test segments will carry over different amounts of slurry to the upper demister.

Although it appears that the DBA was not particularly effective in preventing solids from accumulating on the upper demister sections, some conclusions may be drawn from the test results:

- With the same sulfur fuel, the improved SO_2 removal efficiency (when using DBA) of the absorber vessels will permit operation of the scrubber at lower gas velocities and less carryover of slurry and pluggage resulting from the carryover.

- The hard crystalline scale on the upper demisters is not likely to be reduced by lower gas velocities and may require modification of the demister wash system.

- Some method of directly washing the upper demister on-line (preferably on an intermittent basis to reduce reheat load) may help the removal of both hard and soft types of solids buildup.

LIMESTONE UTILIZATION

Limestone stoichiometric ratio values were determined before and during the DBA tests. During the baseline period of June 11 to July 22, 1984, the average limestone stoichiometric ratio was 1.19 in Recycle Tank B and 1.19 in the filter cake. During the DBA test period, the average limestone stoichiometric ratio was 1.18 in Recycle Tank B and 1.18 in the filter cake. No significant increase or decrease in stoichiometric ratio values can be attributed to the use of DBA. This observation is unique to the Petersburg Unit 3 FGD system in that many of the utilities that tested DBA found dramatic improvements in limestone utilization. The reason that use of DBA did not affect limestone utilization at Petersburg Unit 3 is that during the DBA test, the limestone was of high quality and fine grind.

SO_2 REMOVAL EFFICIENCY ENHANCEMENT

The addition of DBA clearly improved SO_2 removal efficiency in the absorber modules and therefore overall SO_2 removal efficiency of the FGD system. Table 2 summarizes some key data which demonstrate the improved SO_2 removal. Some module SO_2 removal efficiencies were as high as 97 percent (for example, on July 24, 1984 at about 500 ppm DBA); however, other modules were at 75 percent removal efficiency. This inherent variability among the modules was not predictable over periods of up to several days, although the average performance of the four absorber modules over a longer averaging time, e.g., 30 days, is expected to improve.

Some specific short-term results of particular interest are highlighted below:

- 0 to 500 ppm DBA. A difference was observed on the first day of DBA addition. The average module efficiency ranged from 68 to 82 percent before addition of DBA improved to a range of 85 to 96 percent after approximately 500 ppm adipic was slugged to the recycle tanks. This increase in SO_2 removal was observed within 10 to 20 minutes of slugging each of the recycle tanks. On July 23, 1984, Unit 3's boiler was kept at full load, booster fan vanes were kept at 85 percent, none of the spare recycle pumps were run, and pH was controlled to 6.0 (±.1). The coal sulfur content averaged 2.7 percent (as burned), ranging from 2.5 to 3.0 percent.

  An improvement can also be seen by comparing the operation of July 19, 1984, with 2.4 to 3.2 (average 2.8 percent as burned) sulfur fuel without DBA at high pH (greater than 6.0) and all spare recycle pumps running, versus later operation on July 23 1984, with DBA, pH = 6.0, and no spare recycle pumps in operation.

- 500 ppm DBA. At about 500 ppm adipic acid concentration the module efficiencies were in the 85 to 96 percent range at pH = 6.0 and of 74 to 97 percent range with pH = 5.8, with 85 percent booster fan vane settings. On July 24, 1984, the sulfur content of the coal averaged 2.2 percent (as burned), ranging from 2.0 to 2.4 percent.

- 1000 ppm DBA. At 1,000 ppm, the module efficiencies improved to about 90 percent (averaging from 84 to 99 percent) even at pH 5.8, still with no spare recycle pumps running. The sulfur content of the coal ranged from 2.3 to 3.4 percent, averaging 3 percent (as burned).

- 2000 ppm DBA. The scrubber was operated for one day with a DBA concentration of 2000 ppm. Based on very limited data at one operating point (pH = 5.8 and booster fan vanes set at 6.0 to 70 percent), it appears that the module efficiencies increase between 1 to 22 percent when compared to operation without DBA (pH over 6.0, booster fan vanes at 100 percent). The coal sulfur averaged 2.6 (as burned) percent on that day.

In Table 2, "FGD System Efficiency" is the overall efficiency of the scrubber, calculated from stack monitor data (lb $SO_2/10^6$ Btu) and inlet lb/10^6 Btu derived from fuel analyses.

Also in Table 2, "Recycle Tank pH" was taken from control board readings. The actual (SWEC measured) pH of the recycle tanks were 0.1 or 0.2 pH units lower than the control board readings since the procedure for determining recycle tank pH results in higher readings. The difference was less near pH = 6.0 and greater at pH = 5.6 or pH = 5.8.

EFFECTS ON THICKENER AND VACUUM FILTER PERFORMANCE

The operation of the thickener during the test was definitely affected, but not adversely changed by the short-term addition of DBA to the recycle tanks, even at a high (500 ppm) thickener overflow (reclaim water) concentration. It will be necessary in any long-term use of DBA to monitor the effects on dewatering equipment. In particular, inspection and evaluation should be made in the areas of 1) increased corrosion due to operation at lower pH, 2) possibility of filter cloth blinding, and 3) changes in pumping and polymer addition rates.

During the period of low sulfite-to-sulfate molar ratio (indicating higher oxidation of $CaSO_3$ to $CaSO_4$), there were occasional "spikes" of thickener underflow concentrations to 45 percent and above showing on the recorder in the FGD control room. The high solids concentration transients were very short and not verified by actual samples. The high thickener underflow concentration may result in loss of suction on the thickener underflow pumps or storage of the thickener rake.

The pumps did not trip even after several "high" solids excursions, and the rake drive amperage was actually noticeably lower. The variation in sulfite-to-sulfate concentration did not cause an unacceptable mode of operation.

Another variation in thickener operation was observed in that the thickener underflow solids concentration would drop rapidly (instead of previously normal operation where it would decrease slowly) on pumping to the waste slurry tanks, sometimes from 30 percent to 10 percent in less than an hour. This can be attributed to variation in oxidation (i.e., lower sulfite-to-sulfate molar ratio) which appears not to be caused by DBA addition. The low solids concentration recovers rapidly also, on recirculation of slurry to the thickener feedwell. Since this is not an unrecoverable change (i.e., tripping the thickener rake or underflow pumps), it was not investigated further.

Vacuum filter performance appeared to be the same, although the vacuum filter cake solids increased slightly during DBA use. During the baseline period, the average solids content in the vacuum filter cake was 53.4 weight percent, whereas during the DBA test period of August 5 to August 14, 1984, the average solids content was 59.2 weight percent (solids include water of hydration). The improvement can be partly attributed to the lower sulfite-to-sulfate molar ratio which, again, appears to be caused by changes in pH rather than DBA addition.

One result of the DBA test is that the IUCS sludge stabilization system operated for a longer period of time than before the DBA test. This is caused, for the most part, by the higher sulfur fuel being used in the test period (more SO_2 was removed, consuming more limestone and producing more sludge).

Sometimes, both vacuum filters had to be operated at the same time (ordinarily one is sufficient to keep up with sludge production). The filter cake percent solids did not appear to be reduced or otherwise degraded by this mode of operation. The fly ash and lime feed systems appeared to be adequately sized to handle the increased requirements, and the pug mill was able to mix the higher solids loading. The filtrate pumps, however, were not capable of keeping up with the additional filtrate flow, and the floor of the IUCS building flooded under these high sulfur coal burn conditions.

DECOMPOSITION OF DBA

Tables 1 and 3 present the chemical analysis of samples containing DBA. As presented in Table 1, an analysis of a DBA solution sample (sample 7-23-20M of shipment No. 1) indicates no significant decomposition of the DBA in the storage after over four days of recirculation. This may be due to the very low nitric acid content of the Monsanto DBA. Very low nitric acid content is recommended for long-term operation of a buffer additive system. As presented in Table 3, the percentage of "other organic acids" did not significantly increase, indicating that the DBA may have decomposed to carbon dioxide and water.

Table 4 presents the dry weight percent of each of the DBA species (i.e., adipic, glutaric, and succinic) for the DBA storage tank, recycle tanks, and reclaim water. The data on this table indicate that succinic acid decomposes readily in the environment of the scrubber module (e.g., flue gas environment).

Table 5 presents the dry weight ratio of DBA species in the DBA storage tank, recycle tanks, and reclaim water. This table indicates that the decomposition rate of succinic acid is greater than adipic or glutaric acid and that the decomposition rate of glutaric is slightly greater than adipic acid.

EVALUATION OF DBA USE

The following is a summary of advantages and disadvantages of using DBA in the Petersburg Unit 3 FGD system.

Advantages:

- Short-term improvement in module SO_2 removal efficiency
- Possible higher reliability
- Possible reduction in demister pluggage (although this was not observed)
- Reduction of electrical power consumption

Disadvantages:

- High initial system cost and DBA cost
- No observed improvement in stoichiometric ratio (i.e., no reduction in limestone consumption)
- Possible detrimental effect on materials of construction (which could lower reliability)
- Possible acid safety concerns (although no safety problems occurred during the test)

PROCESS EVALUATION

SWEC performed a process evaluation of the Petersburg Unit 3 FGD system to determine the performance of the limestone grinding circuit and obtain FGD system baseline data. The baseline data allowed SWEC to compare the performance of the FGD system with and without the effects of buffer agent additive. SWEC performed specific sampling, monitoring, and analytical work during this evaluation.

SO_2 REMOVAL WITHOUT DBA

Scrubber performance data were collected during the baseline period (July 16 to July 20, 1984). Of particular interest was the attempt on July 19, 1984, to burn high sulfur coal without DBA. Regulatory compliance was met during this test, but the scrubber had to be operated with very high booster fan inlet vane settings, spare recycle pumps, and high pH, resulting in a lower scrubber reliability.

LIMESTONE QUALITY

The limestone used by IPL during the period of June 11 to August 16, 1984, was of a very good quality. The total $CaCO_3$ ranged from 93 to 97 percent by dry weight, with an average of 95 percent $CaCO_3$. The $MgCO_3$ content of the limestone was very low, ranging from 0.35 to 2.6 percent $MgCO_3$ by dry weight, with an average of 1.2 percent $MgCO_3$.

The inerts (SiO_2, Al_2O_3, dirt, etc.) were as expected for a scrubber quality limestone, ranging from 3.2 to 5.3 percent inerts on a dry basis with an average of 3.8 percent inerts.

The moisture content of the limestone was found to be low, ranging from 0.1 to 2.2 percent by weight. This low moisture content was due to the hot summer environment of the limestone pile and the fact that it rarely rained during the test period.

The limestone reactivity test is a relative test that allows a utility to identify limestone which has nonreactive $CaCO_3$. The limestone reactivity values were good during the test period, the average value being 0.67. The limestone reactivity test was conducted as follows:

- A limestone, ground to pass through a No. 200 sieve and to be retained on a No. 325 sieve, was slurried in distilled water and reacted with a less than stoichiometric amount of hydrochloric acid.
- The acidity pH of the slurry was monitored.
- The time from acid addition to pH recovery to a value of 5.50 was determined.

The sooner the slurry pH reached the value of 5.5, the more reactive was the limestone. A response time of 15 minutes or less was set as the criterion for a stone to be used for FGD purposes. To determine if this criterion was met, the time required for the slurry pH to recover to pH = 5.50 was divided by 15.0 minutes. If the answer was less than 1.0, it was determined that the limestone may be useful for FGD purposes, but should be tested further by more elaborate test methods.

GRIND OF LIMESTONE SLURRY

The limestone slurry fed to the scrubber modules and passing a 325-mesh wet sieve ranged from 74 to 92 percent by weight, with the test period average being 87 percent.

Sieve analysis and particle size distribution data indicate that the ball mill ground the limestone, and the classifiers worked. For example, the order of fineness was as expected: limestone recirculation slurry, classifier overflow, ball mill discharge, and classifer underflow. A comparison of data indicated that the limestone fed to the scrubber was significantly more fine on August 16 than on July 19, 1984.

The particle size of the slurry fed to the limestone slurry storage tank was larger than the particle size of the slurry fed to the scrubber modules. This may have been due to the grinding caused by the pumps and agitator of the limestone slurry storage tank.

LIMESTONE SLURRY SOLIDS CONTENT

From June 13 to July 19, 1984, the average solids content of the limestone slurry that leaves the ball mill and enters the classifiers (ball mill discharge samples) was 52 percent by weight. The average solids content of the limestone slurry that leaves the bottom of the classifiers and returns to the ball mill (classifier underflow) was 58 percent by weight. During this same period, the average solids content of the limestone slurry that leaves the top of the classifier and enters the limestone slurry storage tank (classifier overflow) was 38 percent by weight. The classifiers were performing as expected in that the ratio of classifier underflow to overflow solids percent by weight content varied from 1.25 to 1.8. Based on the average (June 13 and July 10) information, approximately 72 percent of the total weight of slurry that entered the classifiers was returned to the ball mill as classfier underflow. This means that only 32 percent of the total slurry weight that enters the classifiers goes to the limestone slurry storage tank.

If the total limestone solids fed to the ball mill is assumed to be 16 tph, then the limestone solids fed to the limestone slurry storage tank would equal 16 tph, the limestone solids returned to the ball mill would equal 70.5 tph, and the limestone solids discharged from the ball mill (fed to the classifiers) would equal 86.5 tph. In this example, the limestone slurry storage tank receives 45.7 tph slurry, the classifiers are fed 163.2 tph from the ball mill, the classifiers return 117.5 tph slurry to the ball mill, the limestone silo feeds 16 tph limestone, and the makeup water to the ball mill is 29.7 tph. This means that the so-called "16 tph" ball mill actually "grinds" 163.2 tph of slurry.

The specific energy (horsepower hours per short ton of limestone fed at pinion shaft) for the Petersburg Unit 3 ball mill is approximately 31, assuming 100 amp ball mill motor at 90 percent efficiency and 16 tph limestone feed. This value of specific energy is similar to the KVS recommendation for a wet grinding closed-circuit, which produces a product size of 95 percent passing a 325-mesh sieve, with a 3/4 x 0-inch limestone fed at 10.0 kWh/ton limestone work index (1). The Petersburg Unit 3 limestone is usually 3/4 x 0 inch in the summer and 3/4 x 1/4 inch in the winter; the larger sizes are easier to move in freezing conditions. The limestone work index at Petersburg normally varies from 10 to 11.

The solids content of the limestone slurry fed to the scrubbers during the test period ranged from 20 to 36 percent by weight solids, with an average value of 29 percent by weight solids. This range and average percent solids content are considered relatively low when compared to other limestone FGD systems. Burning high sulfur coal resulted in very low solids content of the limestone slurry fed to the scrubbers. This was because water was added to the limestone slurry storage tank to prevent low level.

pH OF LIMESTONE SLURRY FED TO THE SCRUBBERS

The pH of limestone slurry in pure water is usually 9 to 10. The use of DBA lowered the pH of the limestone slurry to an average value of 7.4 in the limestone slurry storage tank from July 30 to August 21, 1985. This lower pH was due to the buffering action of the DBA found in the makeup water of the ball mill circuit (i.e., reclaim water).

FLUE GAS TESTING

Flue gas testing was conducted on July 25 and 26, 1984, by SWEC and Acurex to determine SO_2 levels and booster fan outlet flue gas flow rates and to conduct KVB monitor calibration checks.

SAMPLING AND ANALYTICAL PROCEDURES

Flue gas sampling was conducted in accordance with the U.S. Environmental Protection Agency (EPA) "Standards of Performance for New Stationary Sources," Methods 1 through 4, and 8 (2). A modified Method 8 was used for the SO_2 sampling.

Prior to and following the test runs, velocity traverses were conducted at each inlet gas duct location (3-1 and 3-2). Location 3-1 is the horizontal duct (south side) which is downstream of the common crossover duct and feeds flue gas to the Modules A and B inlets. Location 3-2 is the horizontal duct (north side) which is downstream of the common crossover duct and feeds flue gas to Modules C and D. Each rectangular duct was divided into 20 equal areas, and flue gas velocities and temperatures were measured at each midpoint in accordance with EPA Methods 1 and 2. Flue gas flow rates were calculated from the preliminary and post velocity traverse data. Flue gas moisture content was determined using the volumetric condensate procedure.

Triplicate 20-minute sampling runs were conducted. Flue gases were withdrawn for 20 minutes at a single sampling point.

Laboratory procedures for the determination of SO_2 in the hydrogen peroxide impinger solution were conducted as required in the Federal Register (3).

KVB MONITOR CALIBRATION PROCEDURES

Acurex supplied calibration gases of known SO_2 concentrations. Upon SWEC's signal, Acurex injected the calibration gases into the monitors.

The continuous KVB monitor sampling system sampled the known quantity of calibration gases at programmed intervals. The actual composition of the two bottles of calibration gas contained 407 ppm and 2195 ppm SO_2 by volume with the balance being nitrogen.

FLUE GAS TEST RESULTS

Concentrations are expressed in parts per million volume on a dry weight basis (ppmv (SO_2 (dry)). Concentrations at Location 3-1 ranged from 1,397 to 1,487 ppm and from 1,470 to 1,674 ppm SO_2 at the Location 3-2 inlet. The average of all flue gas test values was 1,513 ppm SO_2 as compared to 1,710 ppm SO_2 for the KVB monitor readings. The KVB monitor readings were consistently higher (averaging 13 percent higher) than the values obtained from flue gas testing.

The average of the Location 3-1 values was 1,450 ppm SO_2 and the average of the Location 3-2 values was 1,576 ppm SO_2. The Location 3-2 values were consistently lower (averaging 8 percent lower) than the Location 3-1 values.

The overall average dry volume composition of the flue gas tested was 1,513 ppm SO_2, 12.4 percent CO_2, 6 percent O_2, and 81.6 percent N_2. The overall average moisture content of the flue gas tested was 9.8 percent H_2O. The overall average molecular weight of the wet flue gas tested was 29.

During the flue gas testing, the booster fan inlet vane setting was 75 percent open for each fan, the average boiler load was 495 MW (net), the average temperature was 314°F, the average booster fan discharge pressure was 17.8 in. (H_2O), and the average amount of flue gas processed by each scrubber module was 570,000 acfm.

KVB MONITOR CALIBRATION RESULTS

A KVB six-point extractive flue gas SO_2 monitor (two inlet and four outlet points) was used as an operator tool to provide information for process adjustments. This was not the certified stack monitor. The KVB monitor was calibrated during July 25 to 26, 1984. Based on average readings, the KVB monitor was accurate within +2.1 percent for the 2000 ppm end and accurate within +12 percent for the 400 ppm end. The KVB monitor read consistently higher values than actual. Based on the results of this calibration period, SWEC and IPL deemed the KVB monitor accurate enough for use during the entire SWEC test period.

COAL ANALYSIS

This section of the paper presents the analysis of the coal burned during the process evaluation and DBA test periods of June 11 to August 15, 1984. The ultimate analysis and sulfur analysis were performed by Commercial Testing and Engineering Company for SWEC.

ULTIMATE ANALYSIS

The following Dulong equation was used to estimate the higher heating value (HHV) expressed in Btu/lb.

$$HHV = 14{,}544(C)+62{,}028(H-O/8)+4050(S)$$

where:

C = Carbon by weight fraction
H = Hydrogen by weight fraction
O = Oxygen by weight fraction
S = Sulfur by weight fraction

The HHV (expressed on a dry basis) of the coal burned during the test periods was very consistent, with a range of 12,631 to 12,935 Btu/lb and an average of 12,785 Btu/lb (on a dry basis). The ratio of chlorine to fluorine (on a weight basis) varied from 3.3 to 62, with an average of 20. The ratio of sulfur to chlorine (on a weight basis) varied from 9.5 to 243, with an average of 95.

Before the start of testing, IPL stockpiled approximately 120 hours of high sulfur coal (Arlen mines). This high sulfur coal was selectively burned during the DBA test period.

SULFUR CONTENT OF COAL

The sulfur content of the coal burned during the period of June 11, to August 23, 1984, was determined. The SO_2 release (lb SO_2 per million Btu) was estimated assuming no sulfur capture in the boiler or electrostatic precipitator and using the last previous Dulong-calculated HHV. The sulfur content varied from 1.92 to 3.66 percent by weight on a dry basis, with an average of 2.8 during the entire test period. The SO_2 into the FGD system varied from 2.97 to 5.78 lb SO_2 per million Btu, with an average of 4.36.

During the period of June 11 to July 11, 1984, the average SO_2 into the FGD system was 3.83 lb SO_2 per million Btu. During the baseline data collection period, the average SO_2 into the FGD system was 4.18 lb SO_2 per million Btu. During the DBA test period (July 23 to August 23, 1984), the average value was 4.6 lb $SO_2/10^6$ Btu to the FGD system.

DAILY AVERAGE PERFORMANCE

During the baseline test period of July 16 to July 22, 1984, the daily average gross generation was 9,980 MWh, and the daily average SO_2 removed by the entire FGD system was 148 tons.

During the DBA test period, of July 23 to August 24, 1984, the daily average gross generation was 9,600 MWh, and the daily average SO_2 removed by the entire FGD system was 169 tons.

SOLIDS CONTENT OF RECYCLE TANKS

The solids content (percent by weight total solids) in the recycle tanks was measured during the entire test period. Recycle Tank A consistently had the lowest total solids content during the entire test period. Recycle Tanks B and C consistently had the highest total solids content during the entire test period. During the entire test period, the average solids content in Recycle Tanks A, B, C, and D were 6.84, 11.29, 11.02, and 9.16 percent by weight, respectively.

A low solids content in a recycle tank means that water is diluting the recycle tank slurry. Water can enter the recycle tank from any or all of the following sources: presaturator flow, recycle pump seal water, limestone slurry makeup, and trap out tray bypass.

LIMESTONE STOICHIOMETRIC RATIO

A comparison of data indicates that during each phase of the test period (i.e., baseline test period and DBA test period), the average limestone stoichiometric ratio was 1.2. This means that there was no apparent savings in limestone by using DBA. IPL has demonstrated that the FGD system can be operated with good limestone utilization without additives.

SULFITE-TO-SULFATE RATIO OF RECYCLE TANK AND FILTER CAKE SOLIDS

The average molar ratio of $CaSO_3$ to $CaSO_4$ for all Recycle Tank B and filter cake samples for the entire test periods was approximately 3, which is a normal value for utility limestone FGD systems.

During the baseline test period, the average $CaSO_3$ to $CaSO_4$ ratio was 4.2 and 3.6 for Recycle Tank B and filter cake samples, respectively; whereas during the DBA test period, the ratio was 2.6 and 2.7 for Recycle Tank B and filter cake samples, respectively. A change from a baseline pH of approximately 6.0 to DBA test period pH of 5.8 resulted in more oxidation of the $CaSO_3$. Increased $CaSO_3$ oxidation at reduced pH is a normal behavior of utility limestone FGD systems.

UPPER DEMISTER SOLIDS ANALYSIS

Analyses were performed on the upper demister solids samples taken during the entire test period. Some samples represented traditional high calcium sulfate scale (long narrow crystals) formed by solubility deposition. Other samples represented solids recycle tank which most likely orginated from carry-up of solids from the scrubber absorber spray zone onto the upper demisters.

Average upper demister solids analysis during the entire test period were 67 percent $CaSO_4 \cdot 2H_2O$ equivalent, 6.6 percent $CaSO_3 \cdot 1/2\ H_2O$ equivalent, 4.2 percent $CaCO_3$, 4.5 percent inerts (SiO_2, Al_2O_3, Fe_2O_3, MgO), and 17.7 percent by weight absorbed water.

CORROSION CAUSED BY SCRUBBER OUTLET DUCTWORK CONDENSATE

The pH of the liquid that leaked out of the scrubber outlet damper ductwork and fell on the exterior surface of the scrubber module and platforms varied from 2.27 to 2.55. An analysis of Module D outlet ductwork condensate indicated that the iron and manganese contents of the acidic liquid were very high (i.e., Fe = 2467 and Mn = 68 ppm by weight specie), which means that the module outlet ductwork condensate corroded the ductwork carbon steel. The module outlet ductwork acid condensate leak was one of the causes of "rain" on the structural steel, platforms, exterior surface of modules, equipment, etc.

pH OF LEAKS ON TOP OF RECYCLE TANKS

The following is a representative pH of liquid leaks that fell onto the top lid of the recycle tank:

Sample	Location	pH
7-20-1A	Leak on Recycle Tank B	3.02

PRESATURATOR SOLIDS CONTENT

The solids content of the presaturator distribution plate, walls, and floor originated from electrostatic precipitator fly ash carry-through, recirculated flue gas, scrubber module splash back, and presaturator spray nozzle water. The solids buildup in the presaturator became so severe that the inlet vertical distribution plate was over 90 percent plugged and the depth of solids on the presaturator floor exceeded 2 feet.

Typical examples of the amount of solids in a presaturator are as follows. On July 22, 1984, approximately 530 buckets of solids were carried out of Presaturator D; assuming an average bucket weight of 35 lb, the total amount of solids was over 9 tons. Also on July 21, 1984, approximately 248 buckets of solids were carried out of Presaturator A which equaled approximately four tons of solids. The resulting pile of solids from Presaturator A at grade equaled approximately 65 cu ft. The cleaning of Presaturator A took approximately 8 hours using four men.

The presaturators at Petersburg Unit 3 needed frequent cleaning; however, they were very difficult to clean. IPL usually used a crew of four to five personnel to shovel the solids into buckets, which were dumped to grade where they were front-end loaded into trucks.

pH OF RECYCLE TANK SLURRY

The pH measured by the (daily) calibrated pH meter in the laboratory trailer was compared with the pH noted by the scrubber control board operator at the approximate time of the sample taken by SWEC.

Comparing some of the laboratory readings with the corresponding control panel readings indicates that actual pH conditions inside the recycle tanks are usually lower than the pH indicated by the control board recorder (the signal to that recorder also controls the limestone slurry makeup valve).

The pH of the recycle tanks ranged from 4.0 to 7.7. The range was usually controlled fairly well to a relative pH variation of ± 0.5 pH unit, but the absolute value of pH, as noted above, was usually lower than recorded on the control panel. Relatively high pH values (6.3 to 6.4) usually reflect a module that has been out of service overnight and limestone allowed to dissolve without SO_2 being added. Low end values were usually a result of plugged limestone slurry feed valves which were not cleared right away. The actual pH may differ from actual conditions in the recycle tank at any time due to the pH sampling procedures used by the plant.

RECLAIM WATER pH MEASUREMENTS

Reclaim water pH measurements were taken. The normal range was 6.1 to 6.5 pH, with no substantial variation during DBA addition. One lower pH of reclaim water period occurred August 2 to August 3, 1984 (down to 5.77 and 5.85, respectively), but this was after some low pH testing (down to pH 5.3 range) of the recycle tank conditions during August 1, 1984. For the most part (except for one reading at 5.96 on August 16, 1984), the pH of the reclaim water during DBA testing was between 6.09 to 6.73, which is comparable to pre-DBA period pHs.

DEMISTER WASH WATER

Demister wash water consisted of a mixture of reclaim water and makeup water (i.e., White River water). White River water pH varied from 7.08 to 8.45 with an average of 8.1 during the test. The average total suspended solids content of the demister wash water was 1.1 percent by weight, which is considered to be very high. The average pH of the demister wash water during the entire test period was 6.3.

BOOSTER FAN MOTOR AMPERAGE AND INLET VANE SETTINGS

Between August 3 and August 8, 1984, SWEC collected data on booster fan motor amperage at various fan inlet vane settings. These were obtained by requesting the FGD system operator to call Unit 3 boiler turbine generator board operators and have them relay current amperage to SWEC.

The best fit of a linear relationship occurred above a 40 percent booster fan vane setting, so data below a 40 percent vane setting were left out of the linear regression. The linear relationship fits were reasonably good, with correlation coefficients $\Gamma = 0.9930$ for BFF-3-1 and $\Gamma = .9799$ for BFF-2.

For BFF-3-1, the relationship between vane setting and amperage draw was for vane settings between 40 and 100 percent open.

amp = 157.0495 + 3.6426 x (% vane set)
n = 12 (number of data points)
$\Gamma = 0.9930$ (correlation coefficient)
Sx = 16.35, Sy = 59.98 (standard deviations of sample)

For BFF-3-2, the following linear relationship is the best fit for vane setting vs amperage draw for vane settings between 40 and 100 percent open.

amp = 235.0277 + 2.3546 x (% vane set)
n = 13
$\Gamma = .9799$
Sx = 16.18, Sy = 38.87

The above equations document the electricity savings that can result from decreasing the amount of flue gas scrubbed. The use of DBA allows utilities to remain in compliance while scrubbing less flue gas.

CONCLUSIONS

As presented in the following sections, the maximum sulfur coal that can be burned at Petersburg Unit 3 and remain in compliance depends on many factors. DBA use improved SO_2 removal efficiency, but the short-term variability in SO_2 removal efficiency makes its use appropriate to plants with a 30-day averaging period (like that for Subpart Da units).

MAXIMUM SULFUR COAL THAT CAN BE BURNED WHEN NOT USING DBA

A review of the baseline test data indicates that Petersburg Unit 3 maintained its current 30-day average SO_2 compliance when the coal sulfur content ranged from 2.37 to 3.16 (as fired percent sulfur), under the loading and operating conditions of the test. This coal can be burned at full load if the spare recycle pumps are employed, booster fan inlet vanes are set at 85 percent, and the module pH is 6.0. The unpredictable short-term variability in SO_2 removal discussed earlier makes it difficult to predict future short-term performance. The limestone grind should be maintained at greater than 90 percent passing a 325-mesh sieve, and the limestone stoichiometric ratio (moles calcium carbonate used/moles SO_2 removed) should be approximately 1.2.

MAXIMUM SULFUR COAL THAT CAN BE BURNED WHEN USING DBA

A review of the DBA test period data indicates that the maximum sulfur coal that can be burned at Petersburg Unit 3, while maintaining its current 30-day SO_2 control and operating with 1,000 ppm by weight adipic equivalent of DBA, was in the range of 2.4 to 3.9 (as fired) percent sulfur coal under conditions existing during the test. This coal can be burned at full load and in compliance if no spare recycle pumps are employed, booster fan inlet vanes are set at 75 percent, and the module pH is 5.8. The ball mill should be operated 24 hours per day with the best grind possible (most likely less than 90 percent passing a 325 mesh). The limestone stoichiometric ratio should be approximately 1.2.

MAXIMUM SULFUR COAL THAT CAN BE BURNED AT PARTIAL LOAD WITH A SPARE SCRUBBER MODULE

IPL instituted a program to replace defective scrubber module isolation dampers. This action may result in the possibility of on-line maintenance of a spare module at near full load. Assuming the use of DBA results in over 90 percent SO_2 removal efficiency in the modules and three scrubber modules are operating, a coal in the range of 2.2 to 2.4 (as fired) percent sulfur can be burned at 500 MW, while the spare scrubber module is cleaned or maintained. DBA test data collected on July 26, 1984, is indicative of the ability of the FGD system to operate at near full load with relatively low sulfur coal, while maintaining SO_2 control using only three scrubber modules.

PERMANENT DBA SYSTEM

IPL insitituted a program to install a permanent winterized DBA system at the Petersburg Unit 3 scrubber to improve the SO_2 removal capability of the scrubber and to observe the effects of long-term use of DBA. Of particular importance are 1) corrosion of scrubber materials, 2) rates of demister pluggage, 3) effects on thickener operation at different polymer dosage rates, 4) possible changes to pumping sequences, 5) vacuum filter performance and filter cloth blinding, 6) water balance changes, and 7) effects of slurry solids content on SO_2 removal efficiency in combination with DBA.

ACKNOWLEDGEMENT

The authors would like to thank the management and scrubber operators of IPL, Monsanto Chemical Company, Acurex Corporation, Commercial Testing & Engineering Company, McKenzie Tank/Truck Lines, and Industrial Contractors, Inc. The hard work and good faith efforts by all personnel involved contributed greatly to the success of the scrubber test.

REQUIRED STATEMENT

The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

REFERENCES

1. Rock Talk Manual 1982 Edition, McCormick-Armstrong Co., Wichita, Kansas, 1982, Table C-2, p. 49.

2. U.S. Environmental Protection Agency. Standards of Performance for Stationary Sources. Federal Register, 40CFR60, Methods 1 through 4, and 8, December 23, 1971 (as amended through July 1 1983).

3. U.S. Environmental Protection Agency. Federal Register, 40CFR60, Method 6, Section 4.3, Sample Analysis.

TABLE 1. SHIPMENTS OF DBA (JULY 19 TO AUGUST 23, 1984)

	Shipment/Lot Number							
	1	1a*	2	3	4	5	6	7
Date Shipped	7/17		7/23	7/29	8/5	8/13	8/19	8/22
Date Received	7/19		7/25	7/30	8/6	8/14	8/20	8/23
DBA content, total wt,%	25.74	25.88	25.25	25.70	25.54	25.51	24.98	25.27
Adipic acid wt%	3.70	3.63	3.77	3.93	3.91	4.69	3.96	3.79
Glutaric acid,wt%	16.66	16.84	16.39	16.55	16.62	15.82	16.02	16.29
Succinic acid,wt%	5.38	5.41	5.09	5.81	5.01	5.00	5.00	5.19
Nitric acid,wt%	0.46	-	0.18	0.41	0.20	0.38	0.39	0.65
lb solution shipped	43,600	-	41,980	42,640	41,680	41,960	38,420	46,000
lb DBA (dry)	11,223	-	10,600	10,958	10,645	10,704	9,597	11,624
Butyric,ppm	11							
Valeric,ppm	20†							
Caproic,ppm	9							
Hydroxy Caproic,ppm	<50							
Boric Acid,ppm		12						
Vanadium,ppm	100.78	105.6						
Copper,ppm	2.89	5.6						
Mn,ppm		0.2						

NOTES:

*Sample removed from storage trailer and analyzed. Sample 7-23-20M taken 16:00 hrs on 7/23/84.

†Valeric acid is reported to be responsible for the bad odor of DBA.

TABLE 2. SO_2 REMOVAL EFFICIENCY ENHANCEMENT

Date	Time	MW	BFF % Setting 3-1,3-2	Coal %S and $\#SO_2/10^6$	Average Module Efficiency and Range	FGD System Efficiency	Apidic ppm (All Recycle Tanks)	Control Board pH Recycle Tank	Total Pumps	Notes
	1030			2.84,4.69						
7-19	1400	527	100,100	2.84,4.71	86.6(82.5-91.5)	76.2	0	5.9-6.5	12	Baseline
	1500	534	100,100	2.84,4.71	86.7(81.5-92.6)	76.7	0	5.9-6.5	12	
	1600	524	100,100	2.84,4.71	86.9(80.6-92.9)	75.5	0	6.1-6.5	12	
	1700	530	100,100	2.84,4.71	89.2(83.3-93.1)	76.4	0	6.1-6.5	12	
	1800	523	100,100	2.84,4.71	89.6(87.5-92.9)	77.2	0	6.1-6.5	12	
	1900	530	100,100	2.84,4.71	84.2(75.9-91.3)	75.9	0	6.0-6.5	12	
	2000	528	73,78	2.84,4.71	86.6(82.1-89.4)	76.4	0	6.0-6.5	12	
7-23	0830	535	85,85	2.70,4.71	77.0(75.5-80.7)	74.0	0	6.0-6.2	8	
	0930	530	85,85	2.70,4.71	73.4(67.9-82.4)	72.5	0	6.0-6.1	8	
	1030	532	85,85	2.70,4.47	76.2(72.0-82.1)	73.2	0	6.0	8	
	1130	532	85,85	2.70,4.47	88.9(79.2-94.2)	75.3	Start	5.8-6.0	8	
	1230	530	85,85	2.70,4.47	94.0(92.3-95.8)	80.9	add DBA	5.9-6.0	8	
	1330	530	85,85	2.70,4.47	92.5(88.0-94.8)	82.0	500-650	6.0-6.1	8	500 ppm
	1430	530	85,85	2.78,4.56	92.9(87.2-95.4)	82.3	500-650	6.0-6.1	8	
	1530	535	85,85	2.78,4.56	91.4(86.4-95.0)	85.8	500-680	6.0	8	
	1630	537	85,85	2.78,4.56	93.0(88.5-94.9)	85.8	520-700	6.0	8	
	1730	524	85,85	2.78,4.56	92.9(88.6-94.7)	83.0	520-720	6.0-6.2	8	
	1830	529	85,85	2.78,4.56	90.7(85.8-94.4)	86.5	530-740	6.0-6.1	8	
	1930	533	85,85	2.78,4.56	90.2(85.0-94.7)	86.8	530-780	5.9-6.0	8	
7-24	0830	530	85,85	2.15,4.56	88.0(75.9-92.5)	80.2	200-820	5.8-6.1	8	500 ppm
	1030	523	85,85	2.15,3.58	84.6(76.4-87.8)	79.3	200-800	5.8-6.2	8	
	1200	510	85,85	2.15,3.58	84.2(73.7-88.9)	78.0	250-760	5.8-6.1	8	
	1330	524	85,85	2.15,3.58	82.3(76.5-91.4)	72.4	270-760	5.7-5.8	8	
	1440	526	90,90	2.15,3.58	86.4(77.8-91.1)	75.1	270-750	5.8	8	
	1450	524	80,80	2.15,3.58	85.8(77.4-91.7)	76.1	290-750	5.8	8	

TABLE 2 (Cont)

Date	Time	MW	BFF % Setting 3-1,3-2	Coal %S and #$SO_2/10^6$	Average Module Efficiency and Range	FGD System Efficiency	Apidic ppm (All Recycle Tanks)	Control Board pH Recycle Tank	Total Pumps	Notes
7-24	1520	525	80,80	2.15,3.58	84.2(77.6-92.4)	75.1	300-740	5.8	8	
	1545	523	70,70	2.15,3.58	85.3(79.8-91.9)	74.3	310-740	5.8	8	
	1608	529	70,70	2.15,3.58	87.4(82.3-93.0)	75.4	320-720	5.8	8	
	1635	529	60,60	2.15,3.58	88.4(75.1-95.9)	72.4	320-720	5.8	8	
	1658	517	60,60	2.15,3.58	88.9(76.4-96.1)	71.0	320-720	5.8	8	
	1720	518	50,50	2.15,3.58	94.8(90.4-97.2)	72.1	320-720	5.8-5.9	8	
	1745	522	50,50	2.15,3.58	94.6(90.2-97.1)	67.0	320-720	5.8-5.9	8	
8-13	1000	500	85,85	2.70,3.58	89.5(84.4-94.6)	81.9	900-1000	5.8	8	1000 ppm
	1030	-		2.70,4.566						
	1330	505	70,70	2.70,4.566	92.4(87.1-99.1)	70.1	960-1000	5.8	6	3 modules
	1430			2.99,4.99						
8-14	1030			3.06,5.13						
	1300	520	88,88		93.3(88.7-97.5)	78.8	1050-1150	5.8	8	1000 ppm
	1430			3.19,5.32						
	1439	520	88,88		91.7(86.5-96.8)	80.4	1050-1140	5.8	8	
	1800	526	75,75		89.2(85.3-94.8)	79.7	1050-1140	5.8	8	
8-24	1000	530	60,70	2.61, --	96.8(96.0-98.1)	--	1800-2000	5.8-6.0	8	2000 ppm
	1312	532	60,70	2.61, --	95.0(93.6-96.8)	--	1500-1900	5.8	8	

TABLE 3 CHEMICAL ANALYSIS OF SAMPLES CONTAINING DBA

Sample	Adip.	Glut.	Succ.	Nitric as NO3	Boric as B	Ca	Mg	Mn	Cl	F	Fe	Cu	V	Other Organic Acids (%)
AGS Mixture (7-23-19M)	3.63%	16.84%	5.41%	754	12	--	--	0.2	--	--	--	5.6	105.6	<1
Vac. Filter Filtrate 7/24	16	66	18	2.3	--	--	--	1.2	--	--	--	0.01	<0.1	<1
Recy. Tk. "C" Slurry 7/24	79	390	78	6.2	--	--	--	16.5	--	--	--	0.10	0.3	<1
Recy. Tk "B" Slurry 7/24	64	293	47	2.1	610	--	--	16.5	--	--	--	0.10	0.3	<1
Recy Tk. "B" 7/23	81	387	75	3.3	--	--	--	18.1	--	--	--	0.10	0.3	<1
Recy. Tk. "D" 7/26	92	319	4	0.1	434	--	--	--	--	--	--	--	--	<1
8/1/6M (RTB)	79	309	4	<0.1	496	--	--	1.8	--	--	--	0.20	<1	<1
8/17M (Reclaim)	42	238	4	<0.1	273	--	--	1.6	--	--	--	0.10	<1	<1
8/2/8M RTB	71	431	8	<0.1	537	--	--	3.9	--	--	--	0.10	<1	<1
8/6/8M RTB	130	505	6	<0.1	405	558	1600	--	--	--	--	0.05	--	<1
8/6/9M Reclaim	78	253	35	<0.1	312	684	1280	--	--	--	--	0.05	--	<1
8/8/9M RTB	86	242	ND	ND	485	356	2900	2.42	1219	21	15	--	--	<1
8/8/23M D-Duct	ND	ND	11	ND	19	162	467	68.00	15	1	2467	--	--	<1
8/13/14M RTB	134	426	7	1.9	673	467	4200	2.20	1472	23	0.76	--	--	<1
8/14/11M Reclaim	72	240	ND	ND	320	472	2267	1.44	767	18	0.22	--	--	<1
8/17/9M RTB	157	489	6	5.0	684	346	6733	1.65	1590	26	0.51	--	--	<1
8/22/7M RTA	69	530	69	ND	316	439	2933	2.98	825	19	1.21	--	--	<1
8/24/8M RTB	291	1015	210	4.9	496	401	2533	2.89	1247	--	--	--	--	<1
8/24/11M Reclaim	120	298	31	ND	268	503	2867	1.96	674	--	--	--	--	<1

Note: All results in ppm by weight of the specie unless otherwise indicated.

TABLE 4. DRY WEIGHT PERCENT OF DBA SPECIES

	DBA In Storage Tank			Recycle Tank			Reclaim Water		
Date	Adipic	Glutaric	Succinic	Adipic	Glutaric	Succinic	Adipic	Glutaric	Succinic
7-23	14.0	65.1	20.9	14.9	71.3	13.8			
7-24	14.0	65.1	20.9	15.0	71.9	13.1	16	66	18
7-26	14.9	64.9	20.2	22.2	76.8	1.0			
8-1	15.5	64.4	20.1	20.2	78.8	1.0	14.8	83.8	1.4
8-2	15.5	64.4	20.1	13.9	84.5	1.6			
8-6	15.5	64.4	20.1	20.3	78.7	1.0	21.3	69.1	9.6
8-8	15.3	65.1	19.6	26.2	73.8	0			
8-13	15.3	65.1	19.6	23.6	75.2	1.2			
8-14	15.3	65.1	19.6				23.1	76.9	0
8-17	18.4	62.0	19.6	24.1	75.0	0.9			
8-22	15.9	64.1	20.0	10.3	79.3	10.3			
8-24	15.0	64.5	20.5	19.2	67.0	13.8	26.7	66.4	6.9
Average Weight Percent in Solid DBA	15.4	64.5	20.1	19.1	75.7	5.2	20.4	72.4	7.2

TABLE 5. WEIGHT RATIO OF DBA SPECIES IN SAMPLE

Date (1984)	DBA In Storage Tank		Recycle Tank		Reclaim Water	
	(Succinic/ Adipic)	(Glutaric/ Adipic)	(Succinic/ Adipic)	(Glutaric/ Adipic)	(Succinic/ Adipic)	(Glutaric/ Adipic)
7-23	1.49	4.64	0.926	4.78		
7-24	1.49	4.64	0.86	4.76	1.12	4.12
7-26	1.35	4.34	0.043	3.47		
8-1	1.30	4.17	0.051	3.91	0.095	5.67
8-2	1.30	4.17	0.113	6.07		
8-6	1.30	4.17	0.046	3.88	0.45	3.24
8-8	1.28	4.25	0	2.81		
8-13	1.28	4.25	0.052	3.18		
8-14	1.28	4.25			0	3.33
8-17	1.07	3.37	0.038	3.11		
8-22	1.26	4.05	1.0	7.68		
8-24	1.37	4.30	0.722	3.49	0.26	2.48
Average Weight Ratio	1.3	4.2	0.35	4.3	0.38	3.8

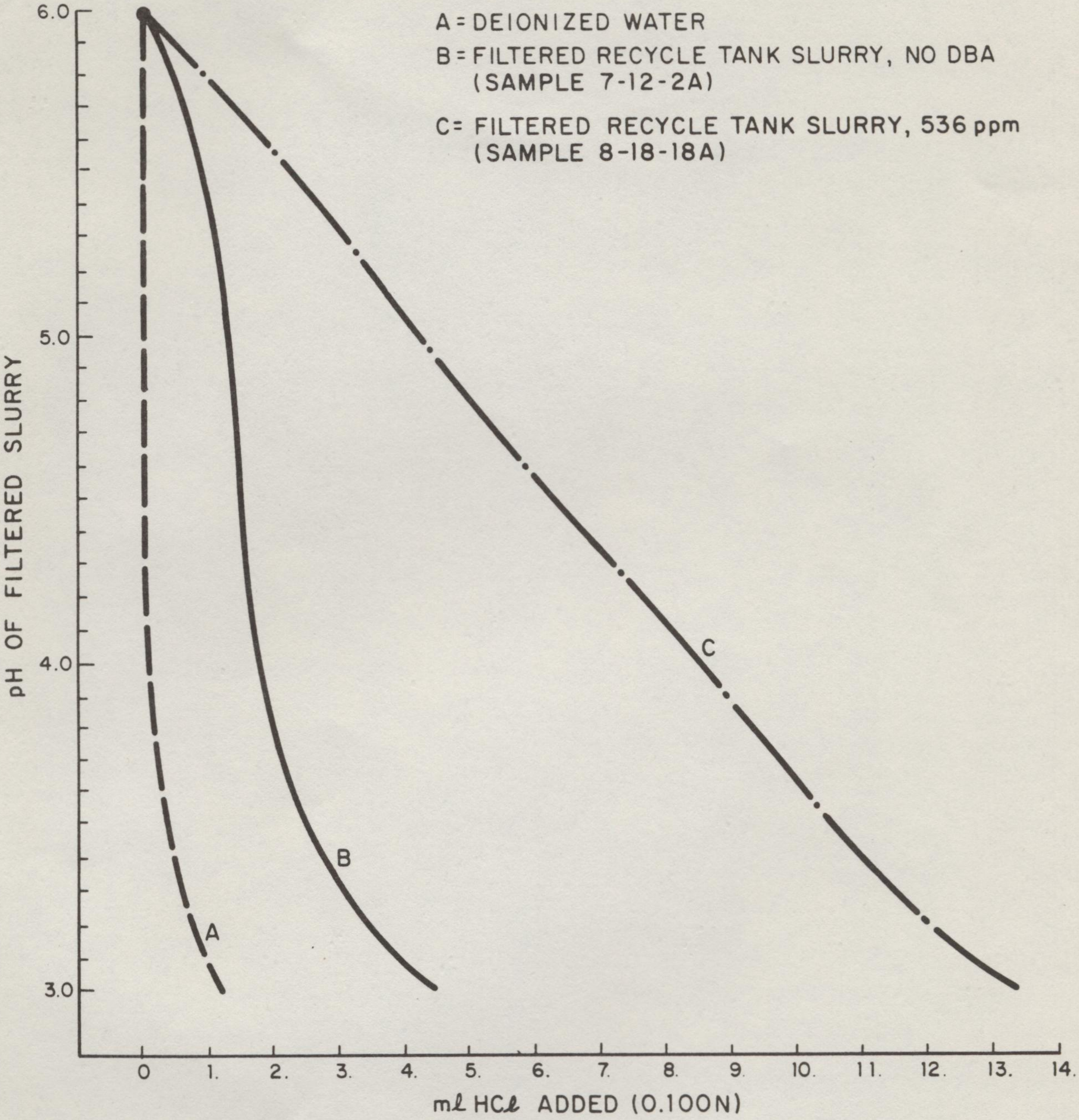

FIGURE 1
TITRATION CURVE FOR RECYCLE TANK SLURRY
WITH AND WITHOUT DBA

APPENDIX I
PROCEDURE FOR ORGANIC ACIDS BY BUFFER CAPACITY TITRATION

DISCUSSION

The method is not specific to adipic acid or to organic acids in general, but measures any buffering compound. Provision can be readily included (not discussed here) to correct for carbonate and sulfite buffering effects.

PROCEDURE*

Calibrate pH meter:

The pH meter should be calibrated daily using both the pH 4 and pH 7 standard buffers. Between samples, the calibration should be checked with the pH 7 buffer.

Fill burets:

(a) Put 1 N NaOH in one buret.

(b) Put 0.1 N HCl in the other buret.

Prepare sample:

(a) Put a magnetic stir bar in a clean and dry 250 ml beaker.

(b) Pipet a 100 ml aliquot of scrubber filtrate into the beaker (the filtrate should be at room temperature).

(c) Place the beaker on the magnetic stirrer, turn on the stirrer, and immerse the electrodes in the sample solution.

(d) Switch the pH meter to OPERATE, wait 1 to 2 minutes for a stable reading, and record the pH of the sample solution.

Adjust sample pH to 6:

(a) Measure the initial level of the NaOH buret to ± 0.01 ml and record as V_I,NaOH·.

(b) SLOWLY add 1 N NaOH dropwise until the pH of the sample solution is ≅6. (Because the NaOH is relatively concentrated, it will be difficult to get a pH of exactly 6.0. If this is the case, it is preferable to overshoot pH 6 slightly and titrate back to pH 6 with HCl according to step (d)).

(c) Rinse the tip of the buret into the sample with a small amount of DI water, record the final buret level as V_F,NaOH, and record the pH of the sample solution.

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*This procedure is based on a general procedure developed and published by Radian Corporation. The procedure was modified slightly.

(d) If pH 6 was exceeded during the addition of NaOH, switch to HCl buret and SLOWLY add 0.1 N HCl dropwise until the pH of the sample solution is 6.00 ± 0.02. Rinse the tip of the buret with a small amount of DI water. Record the pH as pH_I.

Titrate sample to pH3:

(a) Measure the level of the HCl buret to ±0.01 ml and record as V_I,HCL.

(b) SLOWLY add 0.1 N HCl until the pH of the sample solution reaches pH 3.00 (for best results, it is desirable to obtain a final pH of 3.00 ± 0.02).

(c) Rinse the tip of the buret with a small amount of DI water, measure the final level of the HCl buret to ±0.01 ml, and record as $_V F$,HCL.

(d) Record the pH of the sample solution as pH_F.

CALCULATION

Buffer Capacity (Bc)

$$B_c = \frac{C \times V}{\Delta pH \times A}$$

where:

C = normality of HCl in meq/ml
V = volume HCl consumed in ml = V_F,HCL $-V_I$,HCL
A = sample size in 1
$\Delta pH = pH_I - pH_F$

Adipic acid equivalent (ppm by weight in solution)

Adipic acid = 236.45 (B_c - 2.1851) for recycle tank in operation.

Adipic acid = 236.45 (B_c - 1.7283) ppm for recycle tank out of service overnight.

Adipic acid = 236.45 (B_c - 1.4900) ppm for reclaim water.

Adipic acid = 236.45 (B_c - 0.993) ppm for limestone reagent slurry.

Adipic acid = 236.45 (B_c - 1.1300) ppm for demister washwater.

The above equations were developed during the Petersburg Unit 3 FGD system DBA tests of July and August 1984.